3 1151 02692 0045

STORAGE

THE JOHNS HOPKINS UNIVERSITY · BALTIMORE · 1876

THE LIBRARY

ON THE REACTIONS OF ALKYL HALIDES
WITH SODIUM PHENOLATE.

DISSERTATION.

Submitted to the Board of University Studies
of the Johns Hopkins University in
Conformity with the Requirements for the
Degree of
Doctor of Philosophy.

By

H. C. Robertson, Jr.

Baltimore
1910.

CONTENTS.

Acknowledgement . . . . page 2

Introduction . . . . page 3

Experimental

- Introduction . . . . page 10
- Probable causes for decrease in velocity constants . page 13
- Preparation of absolute ethyl alcohol . . . . . page 17
- Purification of alkyl halides page 21
- Purification of phenol . . . page 23
- Standard acids and alkalies page 24
- Temperature regulation . . . page 25
- Conductivity measurements . page 26
- Measurements and calculations of reaction velocities . page 27
- Summary . . . . page 29

Tables of reaction velocities . . . . page 31

Tables of conductivities . . . . page 40

Tabular summary of results . . . . . . page 41

Conclusions . . . . page

Biography . . . . page

ACKNOWLEDGEMENT.

The author takes pleasure in expressing his gratitude to President Remsen, Professor Morse, Professor Jones, Associate Professor Acree and Professor Andrews for instruction in the lecture room and laboratory. Especial thanks are due Associate Professor Acree at whose suggestion this investigation was made.

ON THE REACTIONS OF ALKYL HALIDES WITH SODIUM PHENOLATE.

The problem of how alkyl halides, alkyl nitrates, etc. react with amines, alcoholates, salts of acids and other substances and yield alkyl derivatives is a subject of great importance in organic chemistry. In general, alcohols, organic acids, phenols, etc. react very slowly with alkyl halides. But when a base, or an alcoholate, is added the reaction velocity is increased very greatly. The first important systematic attempt to explain such catalytic reactions was made by Kastle[1] in 1898, who postulated that the catalyzer forms an intermediate salt or compound which reacts further. But Euler[2] gave us in 1901 the first clear cut conception of catalysis in terms of modern physical chemistry when he said[3]: "All of these catalytic phenomena . . . . . depend upon the increase or decrease of one or more of the substances entering into the (non-catalytic) reactions; or, by applying electro-chemical principles to all chemistry, they depend upon the increase of the reacting ions."

---

[1] Amer. Chem. J., 19, 894. Proc. Am. Assn. Adv. Sci., 47, 356. Professor Kastle kindly sent his original manuscript, which was never published in full.

[2] Z. physik. Chem., 32, 348; 36, 405, 663; 40, 501; 47, 356. Z. physicl. Chem., 52, 146.

[3] Z. physik. Chem., 36, 644.

The same idea of an acceleration of enzyme reactions because of an increase in the concentration of the reacting ions from the dissociation of an intermediate double compound of the catalyzer (enzyme) and reacting substances was advanced in 1902 by Acree and Hinkins[1] as a result of work done in 1899-1901. Certain ideas involved in the mechanism of the reactions assumed by Euler and Acree are probably wrong and it remained for Bredig[2] to bring out in January, 1903, and Lapworth[3] in 1904 the central ideas now used in those cases of catalysis in which ions react. The same general ideas have been developed t6o by Acree, by Stieglitz, and by Goldsmith in other lines of work.

Acree and Brunel in 1904-6, and Acree and Johnson in 1907 brought out another principle in catalysis with experimental evidence, namely that in some reactions the acceleration may take place through reactions of both the ionized and the non-ionized salts, the latter sometimes being the chief constituents concerned. It was further brought out by Johnson and Acree that in some (oxime) reactions both the free base and the salts may be concerned in the changes.

Work on various phases of this problem of the alkyl halide reactions has been undertaken in this laboratory by several workers, especially in the tautomeric relationships of the cyclic amides, urazoles and thiourazoles. In general the results indicated that the molecular alkyl halides seemed to react chiefly with the anion of the particular salts stddied although it has several times been pointed out that the undis-

---

1. Am. Chem. J., 28, 370.
2. Z. elek. Chem., 9, 118; 10, 586; 11, 528, and many other articles .
3. Mellor's Statics and Dynamics: pp. 289, 335, 338, 339, 342

sociated salts may also react to a minor extent. The possibility of the reaction of the undissociated salt with the alkyl halide was discussed by Brunel and Acree and was later all the more apparent to us because Johnson and Acree predicted and discovered in the case of the rearrangement of acetyl-chlor-amino-benzene in the presence of acids, the first case of a reaction apparently taking place almost exclusively through the undissociated salt.

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overline{Cl} \rightleftarrows CH_3CONHCl_2C_6H_5 - \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H} + \overline{Cl}$$

The various theories developed by Bruyn and Steger, Nef, and Euler, as to how the alkyl halide may react with the salt were examined by Schadinger and Acree to some extent and it was concluded that at present the safest plan is to consider that the alkyl halide adds, as a molecule, to the salt and forms reversibly a complex salt which can yield the end products. The evidence than at hand seemed to indicate that the alkyl halide reacts chiefly with the anions of the salts then studied and forms a complex anion in very small amount as follows:

$$CH_3I + \overline{An} \rightleftarrows CH_3I.\overline{An} \longrightarrow CH_3An + \overline{I}$$

In the same way the alkyl halide could unite with the molecules, or, since $M \times An = K \times MAn$, with the cations and anions together and form a complex molecule which could yield the end products as follows:

$$CH_3I + \left\{\begin{matrix} \overset{+}{M} + \overset{-}{An} \\ \text{or} \\ MAn \end{matrix}\right\} \rightleftarrows CH_3I.MAn \longrightarrow CH_3An + MI$$

Special conductivity experiments seemed to show that not very much complex salt could be present at any moment, so the small amount must have a large velocity of decomposition.

In order to study more closely the mechanism of the reaction of alkyl halides with the thiourazole salts, Dr. F. M. Rogers continued for a short time the work begun by S~~c~~hadinger,[1] and secured evidence that in ordinary "absolute" alcohol both the urazole ions and the undissociated urazole salt are concerned in the reaction with the alkyl halide. It was seen however that real trustworthy data can be secured only when we use alcohol containing no more than a very few hundredths of a per cent of such impurities as water, salts, etc. It has been shown by some of us in work in this laboratory, and by Goldsmidt,[2] Lapworth,[3] Bredig and Fraenkel,[4] Kailan,[5] Gyr,[6] and others, that water, even in small amounts in some cases, may change the reaction velocities very much. We have therefore shifted our studies to the reactions involved when sodium phenolate reacts with methyl and ethyl iodides in practically absolute alcohol, a transformation studied by Conrad and Brueckner[7] in ordinary "absolute" alcoholic solutions.

---

1. Ber. d. chem. Ges., 41, 3227, 3228, Am. chem. J., 41, 457, 483.
2. Ber. d. Chem. Ges., 39, 711; Z. physik. Chem., 60, 728.
3. J. Chem. Soc., 93, 2163, 2187; Proc. Chem. Soc., 24, 101, 152.
4. Biochem. Z., 6, 308. Z. physik. Chem., 60, 202.
5. Sitzung. Wien, 116, II, 55. Ber. d. chem. Ges., 39, 1055.
6. Ber. d. chem. Ges., 41, 4322.
7. Z. physik. Chem., 7, 274.

The reactions proceed smoothly at 25° and 35° and the constants remain very regular throughout a large part of the transformation. The constants become slightly smaller toward the end of the change, probably because some of the alkyl halide escapes through the stoppers closing the flasks containing the reaction mixture and because a small amount of the alkyl halide may form an olefine by a monomolecular reaction. We have therefore disregarded the small decrease in the constants toward the end of the reaction and have considered the apparent force of the main reaction, which certainly seems to be bimolecular.

If there are two reactions going on side by side as outlined above we should have the following equations:

$$\frac{dx}{dt} = K_{trans}\mathcal{L}(A - x)(B - x) + K'_{trans}\mathcal{L}^2(A - x)(B - x)$$

$$= (K_{trans}\mathcal{L} + K'_{trans}\mathcal{L}^2)\,(A - x)(B - x)$$

$$= \left\{K_{trans}\mathcal{L} + K_{ion}K'_{trans}(1 - \mathcal{L})\right\}(A - x)(B - x)$$

$$= \left\{K_{trans}\mathcal{L} + K''_{trans}(1 - \mathcal{L})\right\}(A - x)(B - x) \text{ or}$$

$$K = K_{trans}\mathcal{L} + K''_{trans}(1 - \mathcal{L}) = \frac{x}{t(A - x)A},$$

if x = 0 when t = 0.

It is evident, then, that when the reaction velocities and conductivities are measured in various concentrations we have variations in $\mathcal{L}$, $1-\mathcal{L}$, A and B, and hence we can determine the values of K_{trans} and K''_{trans} from the series of simultaneous equations obtained by equating the values of K observed against the corresponding values of $K_{trans}\mathcal{L} + K''_{trans}(1-\mathcal{L})$. When this is done very concordant values for K_{trans} and K''_{trans} are obtained, the variation being only about 2 per cent even when A and B vary 2000 per cent and the beginning value of $\mathcal{L}$ is increased 500 per cent. This seems to show then that we have a clean cut case of two simple reactions taking place side by side, with no special catalytic effect to cause uncertainties in the methods or conclusions. Of course other methods of interpretation of the results are apparent to us, and we shall investigate these further; but at present we shall interpret these reactions in the simple manner indicated above.

$$CH_3I + \bar{O}C_6H_5 \rightleftarrows \bar{I} + CH_3OC_6H_5, \text{ and} \quad (1)$$

$$CH_3I + NaOC_6H_5 \longrightarrow NaI + CH_3OC_6H_5. \quad (2)$$

We shall next study the action of alkyl halides with other phenolates in order to see whether the velocity of the ionic reaction (1) is the same in all cases and to see how the velocity of the molecular reaction (2) varies with the dif-

ferent cations. This second step of the problem is of the very greatest importance, as it will allow us to correlate experimentally the energy changes involved, such as the heat of reaction with the heats of formation of the reacting substances and the end products. This point of view has been dwelt on most brilliantly not only by our physical chemical colleagues, but especially by Michael for the organic chemists, and evidence on this problem will be most welcome. An exactly analogous *molecular reaction* has been studied in this laboratory by Johnson, who showed that the velocity varies very greatly when we have different anions, **An**, in the *undissociated compounds* involved in this reaction.

$$CH_3CONHBrAnC_6H_5 \longrightarrow CH_3CONHC_6H_4Br + HAn$$

EXPERIMENTAL.

Introduction. Conrad and Brückner[1] have already studied the reactions of sodium phenolate with alkyl halides, but their work with those compounds was not very extensive. The methods used by them in their study of reaction velocities have been somewhat modified in details which seemed to involve sources of error. These investigators, having made up solutions of phenolates and of alkyl halides of the desired strength, mixed their entire solutions at one time in a large flask and, at the expiration of the desired time-period, pipetted out portions and titrated these. The procedure necessitated opening the flask containing the reaction-mixture a number of times, and rendered liable a loss of the volatile alkyl halide, particularly at the relatively high temperatures. It has seemed preferable to vary this procedure and carry out each individual reaction in a separate small flask of a capacity only slightly larger than the volume of solution to be introduced. In this way possible loss of alkyl halide by volatilization is avoided.

Solutions of sodium phenolate were made up as follows: A solution of sodium ethylate having twice the strength desired for the sodium phenolate was prepared by dissolving clean sodium in absolute alcohol at 0°. A solution of similar strength of dry phenol in alcohol was also

---

[1] Z. physik. Chem., 7, 274.

prepared. By mixing equal volumes of the two solutions, a solution of sodium phenolate of the desired strength was obtained. The contraction on mixing the two solutions is very small, but any loss in volume may be made up by diluting to the mark of the flask with alcohol, if a calibrated measuring flask is used to receive the mixed solutions.

Conrad and Brückner, in studying the reactions of phenolates, made up their solutions in a similar way. They assumed, however, that when sodium ethylate is mixed with its molecular equivalent of phenol, the reaction takes place as below:

$$C_2H_5ONa + C_6H_5OH \rightleftarrows C_6H_5ONa + C_2H_5OH$$

and that the reverse reaction is inappreciable.

It was found, however, in the present investigation that such is probably not the case. On mixing equivalents of sodium ethylate and phenol, solutions of sodium phenolate were obtained which did not give satisfactory constants when reacting with alkyl halides. There was a steady decline in the reaction velocity even in short time- ✓ periods. Tables I and II illustrate this fact. The logical conclusion is that not all of the sodium ethylate has been converted into phenolate, and that we have the two substances reacting at the same time with the alkyl halide. Since the velocity constant of sodium ethylate is about three times that of the phenolate, it disappears more rap-

ly. This would account for the decrease observed.

It was found that on the addition of an excess of phenol better constants were obtained. This is noticeable when only 1 per cent excess is added. (Tables XII and XIII). On comparing these values, however, with those in which no excess of phenol is used, we see that the former are somewhat lower in numerical value. This led to the addition of more phenol and it was found that the decrease in velocity constant was very great when large quantities of phenol were added. Tables I to X and XII and XIII show the effects obtained by the addition of from 1 per cent to 30 per cent excess of phenol.

A study of the rise in boiling point caused by addition of varying excesses of phenol to a normal solution of sodium phenolate in absolute alcoholhas been made. This should throw light on the subject by showing whether or not there is a double salt formation when an excess of phenol is added to the solution of sodium phenolate. It was found that there was no appreciable amount of double salt present at the boiling temperature of the solution, since the rise of boiling point was nearly proportional to the molecular excess added. It is possible that some double salt might be present at the temperatures at which the reactions were carried out, and that this is almost completely broken down at the boiling temperature. The question will be investigated further. A study of the

change in viscosity, caused by the addition of varying excesses of phenol, must be made before any explanation of the phenomenon could be attempted.

In Figure I a curve has been drawn showing graphically the relation between velocity of reaction and excess of phenol. The data is derived from Tables I to X and XII and XIII. These values are all for 1 N solutions of sodium phenolate and methyl iodide at 25°.

It seems that, in preparing solutions of sodium phenolate as described above, it is necessary to add at least a slight excess of phenol in order to convert all the sodium ethylate into phenolate. In all my reactions I have therefore added an excess of one per cent over the calculated quantity of phenol. It is seen from Tables I and XII that the numerical values of the velocity constants are only slightly lowered by the addition of this small excess.

Probable causes for the decrease in velocity constants as the reactions near completion. In practically all the reactions of the alkyl halides that have been studied it has been found that there is a steady decrease in the velocity constants as the reaction progresses. It is seldom possible to obtain concordant values after fifty per cent of the reacting substances have undergone change. It will be seen from my tables that I have relied mainly on the first half of the reactions for the best constants.

The cause of this decrease in velocity constants has been attributed by many investigators to a loss of alkyl halide during the course of the reaction. The question has been taken up in the present investigation and it is certain that only a small part of this decrease can be attributed to ~~the above~~ this source.

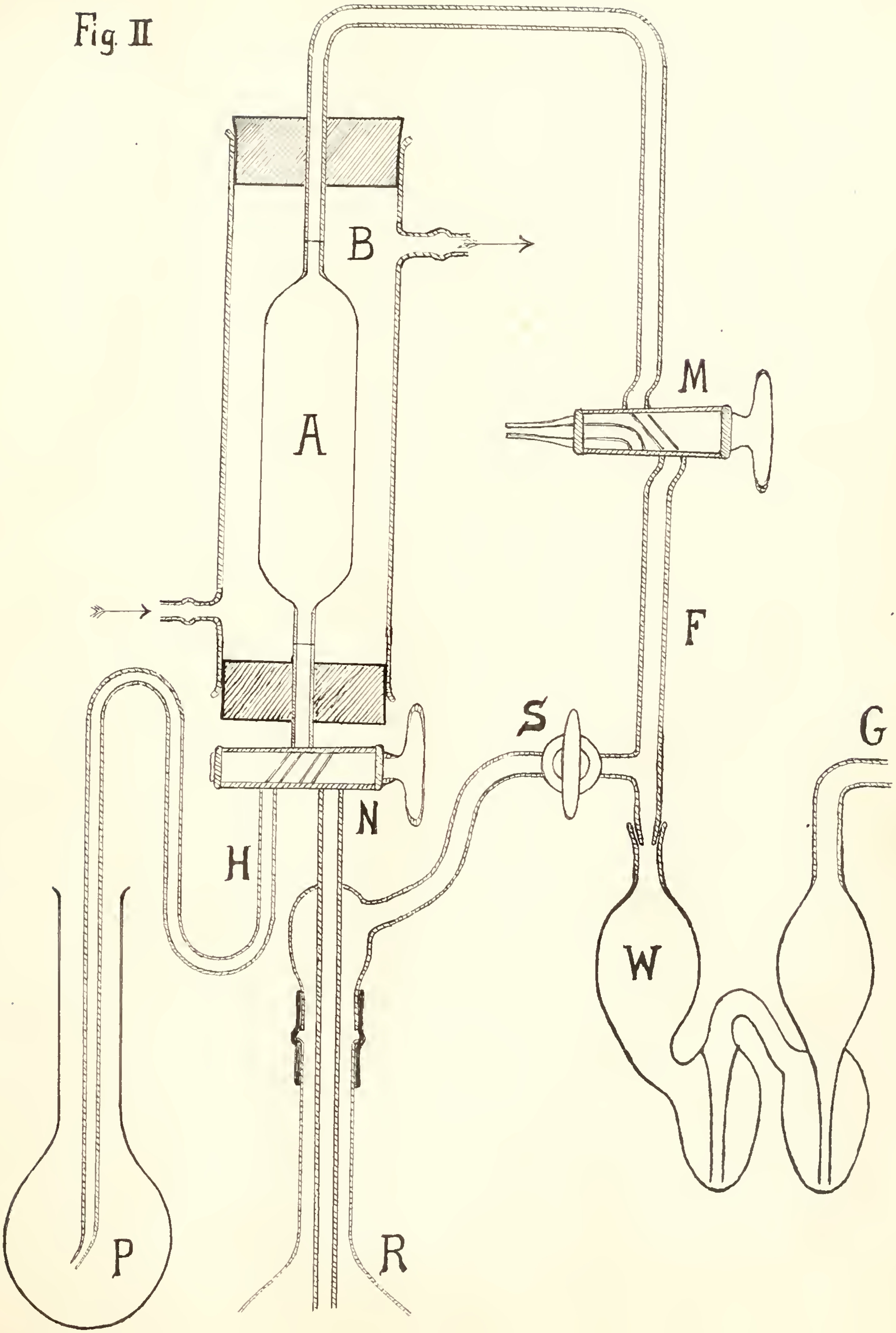
Solutions of methyl iodide (this being one of the most volatile alkyl halides) were used for a study of the question. Standard solutions were prepared by weighing into a measuring flask nearly full of absolute alcohol a slight excess over the calculated amount of methyl iodide. The volume of alcohol necessary to bring the solution to the desired strength was then added from a pipette, both solution and alcohol of course being at the correct temperature.

A normal solution of methyl iodide was prepared as above and two 10 c.c. portions were withdrawn by suction with an ordinary pipette. Each of these was added to an aqueous solution of silver nitrate in a tube which was at once sealed and heated at 60° for 24 hours. The results of these analyses showed that about one per cent of the alkyl halide had been lost in the process of making up and transferring the solutions.

These results were confirmed by other analyses, in some cases the loss of methyl iodide being even larger. It should be stated that the alkyl halide had been previously analyzed and was undoubtedly quite pure.

From these experiments it was realized that unless

Fig. II



precautions were taken to eliminate the error involved by loss of alkyl halide, the velocity constants in long time periods might be seriously affected. A special form of pipette has been therefore devised which has proved itself invaluable in working with the alkyl halides and volatile liquids in general. Figure II shows in detail the construction and mechanism of this apparatus.

The pipette (A) is surrounded by a jacket (B) through which water of the desired temperature is made to circulate. The solution to be measured out is contained in flask (R) which, together with the wash-bulb (W) is immersed in the constant temperature bath. A blowing bulb is attached at (G). The wash-~~tube~~ bulb (W) is supplied with a small quantity of the solution to be measured out.

To fill the pipette, stopcock (N) is turned so as to connect (A) with (R), the stopcock (S) is opened and (M) is turned so as to furnish an outlet from (A) to the air. On pressing the blowing bulb, the solution in (R) is forced into the pipette, the air which reaches the solution in (R) being saturated with the vapor of the alkyl halide solution by passage through the wash-bulb (W). To deliver the pipette, stopcock (M) is turned so as to connect (P) with (A). Stopcock (S) is closed, and (N) is turned so as to connect (A) with (N). The liquid flows into the flask (P) and the pipette is at the same time filled, with air saturated with the vapor of the alkyl halide solution. This apparatus has been of great service in the work with methyl iodide.

When it is used, the loss from volatilization is much less than is occasioned by the use of an ordinary pipette. Analyses were made of three 10 c.c. portions of methyl iodide measured out by the aid of the above device. The results are given below. The alkyl halide solution was 0.3 per cent stronger than normal.

Analyses	Percentage Normal Found	Percentage Normal calculated
1	100.21	100.30
2	100.12	100.30
3	100.05	100.30

It is evident that the error involved when the apparatus described above is used, is much less than with the ordinary form of pipette.

Experiments were carried out to determine whether alkyl halide is lost from the reaction flasks after they are stoppered and placed in the constant temperature baths. It was found that their weight did not decrease perceptibly even after standing a week.

It is evident that the decrease in velocity constants as the time periods become longer can not be attributed solely to loss of alkyl halide. At present it seems most probable that it is mainly due to a monomolecular side-reaction in which an olefine is formed. 2

Preparation of Absolute Ethyl Alcohol. With the exception of a few series of reactions carried out to determine the effect of traces of water on reaction velocity, the solvent used was invariably absolute alcohol. The work of numerous investigators[1] has shown that the effect of water on the velocity of reactions of this type is a very important factor, and one that must be considered if accurate measurements are to be made. While the effect of traces of water on reactions between sodium phenolate and alkyl halides is not so great as in some other cases, it is nevertheless quite appreciable, and it seemed advisable to eliminate this factor by the use of solvents as free from moisture as it was practicable to obtain them. The dehydration of ethyl alcohol is a comparatively simple matter. The best commercial article was boiled several days with 400 grams of calcium oxide per liter of alcohol. After distillation, the treatment with calcium oxide was repeated, by using a smaller proportion than before. The last traces of moisture were removed by digesting the alcohol with turnings of metallic calcium at 40°. At this temperature, the metal is only slowly acted upon by alcohol, and the dehydration is very effective. After the first portion of calcium has passed into solution, second and third portions of about 10 grams or less per liter may be added and allowed to react at a moderate tem-

---

1. Goldschmidt and Sunde, Ber. d. chem. Ges., 39, 711; Joseph Cyr, Ber. d. chem. Ges., 41, 4322; Lapworth, J. Chem. Soc., 93, 2163, and many others.

perature . Such treatment will always be found sufficient to produce alcohol of a high degree of dehydration.

Before treating with metallic calcium as above, the alcohol was invariably digested with 10 grams of silver nitrate per liter and distilled, after which it gave no test for aldehydes.

It was found, in general, that the first treatment with calcium oxide gave alcohol of about 99.7 per cent. A second similar treatment in some cases gave alcohol of 99.99 per cent purity. This was, however, only attained after several days digestion at boiling temperature. It is much more convenient to remove the last traces of moisture with metallic calcium.

It appears that at present specific gravity determinations made with a carefully calibrated pycnometer, of at least 40 c.c. capacity, give the surest evidence of the dehydration of alcohol. The Critical Temperature of Solution in kerosene, advocated by some investigators[1], is hardly applicable as a test for absolute quantities of water, though it is certainly of great value in determining relative proportions. There is necessarily, considerable variation, both in composition and dryness, between different samples of kerosene, and both factors are of essential importance. It was found that alcohol of specific

---

[1] L. W. Andrews, J. Am. Chem. Soc., 30, 353.

gravity 0.78510 $\frac{25^\circ}{4^\circ}$ when mixed in equal volumes with commercial kerosene which had not been dried or distilled, gave a C.T.S. of 4°.02. With equal volumes of the same kerosene dried with calcium chloride and distilled the C.T.S. was -4°. Andrews suggests that kerosene used for this purpose should be first treated by passing steam through it for a time to free it from its most volatile constituents and then dried and used. I have found that the C.T.S. of alcohol in kerosene so treated will vary greatly with the length of time that steam is passed through the kerosene. As an extreme instance, kerosene treated in this way for two days, when dried and distilled gave with 100 per cent alcohol a C.T.S. = 12°, while the portion of the oil which was volatile with water vapor, when dried, showed no cloudiness when mixed with an equal volume of 100 per cent alcohol at a temperature of -8°. It is evident that the low boiling constituents of kerosene give with alcohol a much lower C.T.S. than the high boiling constituents and consequently variations in composition of kerosene will give corresponding variations of Critical Solution Temperature. To use this method as a criterion of dehydration of alcohol would be harily safe until one had set a standard for his particular sample of kerosene. I have relied entirely on the specific gravity method.

The pycnometer used for the determination of specific gravity was of the Ostwald-Sprengel type and had

a capacity of approximately 50 c.c. It was provided with close-fitting, ground-glass caps to prevent evaporation during weighing. This pycnometer was carefully calibrated several times and its capacity was known with a probable error of 0.0002 c.c. It seems that little is to be gained by the use of a pycnometer larger than this, unless one has a balance which is exceptionally sensitive under a heavy load. After bringing the pycnometer and its contents to the temperature of the bath, it was adjusted, wiped dry and allowed to stand in the balance case for five minutes, when its weight was taken.

A number of samples of alcohol have been dehydrated as above and their specific gravities determined. The following values have been obtained within the last few months. In each case the alcohol was treated with silver nitrate and with calcium oxide twice besides the further treatment with calcium turnings.

Sample (1), treated with four portions of metallic calcium, Sp.Gr.= 0.785068.

Sample (2), treated with calcium three times, Sp.Gr.= 0.785089

Sample (3), dried with calcium three times, Sp.Gr.= 0.785084

Sample (4), dried with calcium three times, Sp.Gr.= 0.785084

Sample (5), dried with calcium three times, Sp.Gr.= 0.785084

Sample (6), dried with calcium three times, Sp.Gr.= 0.785084

Sample (7), dried with calcium four
times (middle portion of
distillate) Sp.Gr.=

Sample (8), dried with calcium six
times (middle portion of
distillate) Sp.Gr.=

It seems that under ordinary conditions, anhydrous alcohol, obtained by the action of quick lime and calcium turnings on the commercial article, has a specific gravity of about 0.785085. By very complete dehydration and by fractional distillation somewhat lower figures may be obtained.

From this work it seems that the most probable value for the specific gravity of alcohol is $\frac{25^\circ}{4^\circ}$. It should be stated that the specific gravity of water at 25° used for the above calculations was 0.997071, the value obtained by Thiesen[1] and that the temperatures are on the hydrogen scale. Work on the physical constants of alcohol will be continued in this laboratory.

Purification of Alkyl Halides. Ethyl Iodide. For the preparation of pure ethyl iodide, the best obtainable iodine was added to red phosphorus in 100 per cent alcohol. After drying for a few minutes with calcium chloride, the dehydration was completed with a small quantity of resublimed phosphorus pentoxide. The alkyl halide was subsequently redistilled several times and thus obtained in good condition.

---

1. Wiss. Abh. d. phys.-techn. Reichs-anst., 3, 68, 1900.

The effect of light on the decomposition of these compounds being very marked, containing vessels of brown glass were used. By the addition of a few drops of mercury, ethyl iodide may be kept entirely colorless. That there is no appreciable interaction between the two was shown by boiling ethyl iodide, under a return condenser, for three days with one fifth its volume of mercury. Even with this vigorous treatment the action is slight for it was found that only a little mercurous iodide was formed. On distilling the alkyl halide, a trace of mercury was found in the distillate. It is probable that at boiling temperature, a little mercury ethyl is formed, but, at ordinary temperatures, the quantity is not appreciable.

The boiling point of ethyl iodide prepared as above was found to be 72°.4 under 760 mm. pressure.

Methyl Iodide. The methyl alcohol used in the preparation of methyl iodide contained about 0.1 per cent water. Only the best iodine was used. Phosphorus pentoxide was used to remove the last traces of water. After drying and redistilling, the methyl iodide was kept in dark bottles over a little mercury.

Since very discordant values are given by different authorities[1] for the boiling point and specific gravity of methyl iodide, careful determinations of both

---

[1] Dobriner, Ann. d. Chem., 243, 23.
Perkin, J. f. prakt. Chem. (2) 31, 500.
Ipatiew, J. f. prakt. Chem. (2) 53, 275.

values were made. The thermometer used for the boiling point determination was graduated in tenths of a degree. This thermometer was subsequently checked against a standard platinum resistance thermometer. The following values were obtained:

Sample I. Dried with phosphorus pentoxide and
redistilled four times.
B.P. = 42°32 -- 42°34 under 759.35 mm. pressure.

Sample II. Dried as above and redistilled twice.
B.P. = 42°25 -- 42°31 under 757.65 mm. pressure.

The specific gravity of sample (II) was found to be $2.2619 \frac{25^{\circ}}{4^{\circ}}$.

Analysis:

0.7978 gram methyl iodide gave 1.3200 gram silver iodide.

	Gram found	Gram calculated
I	0.7135	0.7133

Phenol. The phenol used was Kahlbaum's best. It was twice redistilled and boiled from 180°.1-.2 uncorrected. After distillation it was pulverized and dried in vacuum desiccators over concentrated sulphuric acid for several weeks. After this treatment, it is improbable that more than traces of water were present. In making up solutions with phenol, care was taken not to expose it to the air more than was necessary, since it is quite hygroscopic.

Standard Acids and Alkalies. Hydrochloric acid was used for all titrations. It was standardized in several ways all of which agreed satisfactorily.

The method of Acree and Brunel[1] is convenient and gives very satisfactory results. Dry, gaseous hydrochloric acid was passed into a flask containing a weighed quantity of water, precautions being taken to prevent loss of water vapor. The amount of acid absorbed was determined directly by weight, and the solution thus obtained used as a standard in making up a large quantity of normal acid.

Standard hydrochloric acid was also prepared by Hulett's method[2], and the results obtained were quite satisfactory. The acids obtained by these two methods were found to check one another within 0.1 per cent. Two gravimetric analyses of hydrochloric acid by Hulett's method were made, one giving 99.97 per cent calculated weight of silver chloride and the other 100.07 per cent calculated.

Standard sodium hydroxide was made from metallic sodium by means of sodium amalgam. It was thought that this gave a somewhat sharper titration with methyl orange than was given by alkalies containing carbonate. The alkali was standardized by titration against standard hydrochloric acid. Methyl orange was invariably used in all titrations.

---

[1] Am. Chem. J., 36, 117.

Temperature Regulation. Constant temperatures were maintained by the use of two baths, one having a capacity of about 450 liters for work at 25°, and the other with a capacity of 40 liters for work at 35°. Both were provided with efficient stirrers and there was no difficulty in keeping their temperatures constant within 0°.01, which was entirely satisfactory for reaction and conductivity work.

In making specific gravity determinations, however, it was necessary to read temperatures somewhat closer than 0°.01. A Beckmann thermometer was therefore compared carefully with the standard and kept in the bath constantly for use in this work. In the pycnometric determinations of alcohol, the temperature was read within several thousandths of a degree and was probably correct within ± 0.004.

The thermometers used in this work have been checked by Dr. B. B. Turner in this laboratory against a standard platinum resistance thermometer of the Dickinson-Mueller type[1] as used in the United States Bureau of Standards, and somewhat modified by Dr. Turner. Our temperature standard is accurate to about ± 0.002 which is much closer than any ordinary mercury thermometer can be read.

---

[1] Bull. U. S. Bur. Stand., Vol. 3, No. 4.

Conductivity Measurements. The cells used were of two types, the Arrhenius form as modified by Jones and Bingham[1] with electrodes fused into ground glass stoppers, being used for the measurement of relatively high conductivities, while, for very dilute solutions, cells were used of the type suggested and described by Turner[2]. These differ from the first form in that they present a very large surface of platinum and the cell constants are quite low, being about 2.0 for the cell used in this investigation. These cells are simple in construction, consisting of three concentric cylinders of platinum, the outer and inner cylinders constituting one electrode, the middle one being the other electrode. The cell is compact and the electrodes being more rigid than in other forms, there is less danger of a change in the cell constant by scraping the electrodes against the sides of the cell in lifting them out.

The bridge wire, resistance box, etc. were carefully calibrated. Three readings of each resistance were taken at different points on the bridge wire and the results were averaged, the mean values being given in Table XXXI. All conductivities are expressed in reciprocal ohms.

---

[1] Amer. Chem. J., 34, 493.
[2] Ibid., 40, 558.

Measurements and Calculations of Reaction Velocities. As has been already stated, I have considered it preferable to carry on each reaction in a small individual flask, rather than to mix the entire volume of solution in one flask and pipette out portions for analysis as desired. The disadvantages of the latter procedure have been discussed.

The reactions were interrupted at the end of the desired time-period by removing the small flask from the bath and pouring its contents into 200 c.c. of cold distilled water after which the titration with standard hydrochloric acid was immediately made, and the amount of unchanged sodium phenolate thus determined. It should be said that, in general, the acid used was one-fifth as strong as the sodium phenolate solution against which it was titrated. It was found by experiment that the above procedure involved no appreciable error, the progress of the reaction being practically reduced to zero by dilution with the large volume of cold water.

In the tables which follow, the constants have been calculated from the equations:

$$(1)\quad AK = \frac{1}{t} \cdot \frac{x}{A - x} \quad \text{(for equivalent masses)}$$

$$(2)\quad K = \frac{1}{t(A - B)} \ln \frac{B(A - x)}{A(B - x)} \quad \text{(for unequal masses)}$$

To compare the two sets of constants, however, it is necessary to alter slightly equation (2)[1] which becomes:

$$K = \frac{1}{t(n - 1)} \ln \frac{B(A - x)}{A(B - x)} \quad \text{where } n = \frac{A}{B}$$

In this way both sets of velocity constants are referred to the same basis and become comparable.

The values given for A represent the actual volumes in cubic centimeters of the sodium phenolate solutions used. Under x is given the number of cubic centimeters of standard acid required for each titration, *referred to the same normality as the sodium phenolate solution used in that particular series of reactions*. These values actually represent the volumes of (A) that have disappeared at the end of each time period. K_n represents the velocity constant for each series when referred to the normal basis. It is obtained by multiplying the constants AK and K by the dilution, in liters, of the sodium phenolate after mixture with the alkyl halide solution.

---

1. Hecht, Conrad and Brückner, Z. f. physik. Chem., 3, 455.

Summary. Tables I to X and Tables XII and XIII illustrate the decrease in velocity of reaction as increasing excesses of phenol are added. This is also shown graphically in Figure I.

Tables XI to XVII show the velocities of reactions of sodium phenolate and methyl iodide at 25° in solutions varying in strength from 2 N to 0.1 N before mixing.

Tables XVIII to XXIV give the velocities of reactions of sodium phenolate and methyl iodide at 35°, in solutions varying from 1 N to 0.05 N before mixing.

Tables XXV to XXX show the velocities of reactions of sodium phenolate and ethyl iodide at 25° and 2 30° in solutions of various dilutions.

Table XXXI is a summary of the conductivity data obtained.

In Table XXXII both the velocity constants given in Tables XI to XVII and the dissociation data derived from the conductivity measurements have been substituted in the equation:

$$K = K_{trans}\alpha + K''_{trans}(1 - \alpha)$$

$$\text{or } K = K_i\alpha + K_m(1 - \alpha)$$

where K_i is the velocity constant of the ionic reaction and K_m is the velocity constant for the molecular reaction. The simultaneous equations so obtained have been

solved in Table XXXIII, the first column of which indicates the two equations that have been used in each case.

It seems that, considering the many possible sources of error, both in reaction work and conductivity measurements, the constants obtained are satisfactory. Although both dissociation and dilution have varied widely, there has been but little variation in these constants.

Effect of Excess of Phenol on Reaction Velocity.

Table I.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(No excess phenol)

A = 10.02 Temp. = 25°

t.	x.	AK.
30	1.28	0.00488
40	1.62	0.00482
50	1.90	0.00468
60	2.16	0.00458
80	2.66	0.00452
100	3.09	0.00446

Average AK = 0.00466

Table II.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(No excess phenol)

A = 10.00 Temp. = 25°

t.	x.	AK.
40	1.62	0.00483
50	1.95	0.00484
60	2.17	0.00462
80	2.70	0.00462
100	3.14	0.00458
140	3.86	0.00449

Average AK = 0.00466

For reactions with 1 per cent excess phenol, see Tables XII and XIII.

Table III.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(2 per cent excess phenol)

A = 10.00 Temp. = 25°

t.	x.	AK.
30	1.22	0.00463
40	1.54	0.00455
50	1.88	0.00463
65	2.31	0.00462
75	2.54	0.00454
90	2.84	0.00441

Average AK = 0.00456

Table IV.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(2 per cent excess phenol)

A = 10.00 Temp. = 25°

t.	x.	AK.
30	1.20	0.00454
40	1.53	0.00451
50	1.86	0.00457
60	2.14	0.00454
70	2.44	0.00460
100	3.09	0.00447

Average AK = 0.00454

Table V.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(5 per cent excess phenol)

A = 10.04 Temp. = 25°

t.	x.	AK.
30	1.15	0.00431
40	1.47	0.00428
50	1.77	0.00428
60	2.06	0.00430
70	2.32	0.00429
90	2.99	0.00428

Average AK = 0.00429

Table VI.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(5 per cent excess phenol)

A = 10.01 Temp. = 25°

t.	x.	AK.
30	1.16	0.00436
40	1.48	0.00434
50	1.79	0.00435
60	2.06	0.00432
100	3.04	0.00436

Average AK = 0.00435

Table VII.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(10 per cent excess phenol)

A = 10.04 Temp. = 25°

t.	x.	AK.
20	0.76	0.00409
30	1.12	0.00418
40	1.42	0.00412
50	1.73	0.00416
60	1.98	0.00409
80	2.48	0.00410

Average AK = 0.00412

Table VIII.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(10 per cent excess phenol)

A = 10.05 Temp. = 25°

t,	x.	AK.
20	0.754	0.00406
30	1.106	0.00412
40	1.44	0.00418
50	1.69	0.00404
60	1.97	0.00406

Average AK = 0.00409

Table IX.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(20 per cent excess phenol)

A = 10.01 Temp. = 25°

t.	x.	AK.
20	0.71	0.00382
40	1.34	0.00386
50	1.65	0.00395
60	1.90	0.00390
90	2.62	0.00395
260	5.05	0.00391

Average AK = 0.00390

Table X.

1 N. Sodium Phenolate and
1 N. Methyl Iodide
(30 per cent excess phenol)

A = 10.01 Temp. = 24°.95

t.	x.	AK.
30	0.99	0.00365
40	1.28	0.00367
50	1.57	0.00372
60	1.80	0.00365
80	2.27	0.00366
100	2.69	0.00367
123	3.10	0.00365

Average AK = 0.00367

Reactions between Sodium Phenolate and Methyl Iodide at 25° and 35°

Table XI.

2 N. Sodium Phenolate and
2 N. Methyl Iodide

A = 10.00 Temp. = 25°

t.	x.	AK.
20	1.33	0.00780
30	1.87	0.00766
40	2.35	0.00767
50	2.78	0.00770
60	3.14	0.00762
80	3.75	0.00750

Average AK = 0.00766

K_n = 0.00766

Table XII.

1 N. Sodium Phenolate and
1 N. Methyl Iodide

A = 10.00 Temp. = 25°

t.	x.	AK.
30	1.24	0.00471
40	1.56	0.00462
51	1.91	0.00462
60	2.18	0.00464
70	2.45	0.00464
80	2.66	0.00452
100	3.14	0.00457

Average AK = 0.00462

K_n = 0.00924

Table XIII.

1 N. Sodium Phenolate and
1 N. Methyl Iodide

A = 9.98 Temp. = 25°

t.	x.	AK.
21	0.91	0.00478
30	1.22	0.00464
40	1.56	0.00463
50	1.88	0.00465
60	2.16	0.00460
80	2.65	0.00452
120	3.52	0.00454

Average AK = 0.00462

K_n = 0.00924

Table XIV.

0.75 N. Sodium Phenolate and
0.75 N. Methyl Iodide

A = 10.00 Temp. = 25°

t.	x.	AK.
30	1.01	0.00375
40	1.28	0.00367
50	1.53	0.00361
60	1.80	0.00366
70	2.03	0.00363

Average AK = 0.00366

K_n = 0.00976

Table XV.

0.5 N. Sodium Phenolate and
0.5 N. Methyl Iodide.

A = 10.00 Temp. = 25°

t.	x.	AK.
30	0.736	0.00265
40	0.98	0.00271
50	1.18	0.00267
60	1.39	0.00269
70	1.56	0.00264
82	1.77	0.00262
150	2.80	0.00259

Average AK = 0.00265

K_n = 0.01060

Table XVI.

0.25 N. Sodium Phenolate and
1 N. Methyl Iodide.

A = 40.00 B = 10.00 Temp. 25°

t.	x.	K.
40	2.22	0.00161
50	2.66	0.00160
60	3.04	0.00157
72	3.50	0.00157
90	4.02	0.00151
100	4.38	0.00153

Average K = 0.00156

K_n = 0.01248

Table XVII.

0.1 N Sodium Phenolate and
0.5 N Methyl Iodide

A = 100.00 B = 20.00 Temp 25°

t.	x.	K.
120	6.90	0.000732
145	8.05	0.000743
160	8.45	0.000720
190	9.50	0.000717
210	10.14	0.000715

Average K = 0.000725

K_n = 0.001550

Table XVIII.

1 N. Sodium Phenolate and
1 N. Methyl Iodide.

A = 9.98 Temp. = 35°

t.	x.	AK.
20	2.18	0.01397
30	2.93	0.01385
40	3.55	0.01381
50	4.08	0.01383
60	4.50	0.01368

Average AK = 0.01383

K_n = 0.02766

Table XIX.

1 N. Sodium Phonolate and
1 N. Methyl Iodide

A = 10.00 Temp. 35°

t.	x.	AK.
30	2.98	0.01412
40	3.60	0.01406
50	4.13	0.01407
60	4.53	0.01381
72	4.96	0.01367
85	5.42	0.01392

Average AK = 0.01394

K_n = 0.02788

Table XX.

0.75 N Sodium Phenolate and
0.75 N Methyl Iodide

A = 9.98 Temp. 35°

t.	x.	AK
20	1.77	0.01078
30	2.45	0.01086
40	3.07	0.01108
50	3.58	0.01117
60	3.97	0.01098
70	4.34	0.01097
100	5.23	0.01101

Average AK = 0.01098

K_n = 0.02928

Table XXI.

0.5 N Sodium Phenolate and
0.5 N Methyl Iodide

A = 9.98 Temp. 35°

t.	x.	AK.
40	2.44	0.00808
50	2.86	0.00803
60	3.21	0.00791
70	3.59	0.00802
80	3.89	0.00798
100	4.39	0.00785

Average AK = 0.00798

K_n = 0.03192

Table XXII.

0.25 N Sodium Phenolate and
0.5 N Methyl Iodide

A = 20.00 B = 10.00 Temp. 35°

t.	x.	K.
20	1.66	0.00474
30	2.42	0.00492
40	3.02	0.00490
50	3.52	0.00481
60	3.95	0.00472
70	4.39	0.00472

Average K = 0.00480

K_n = 0.03840

Table XXIII.

0.1 N Sodium Phenolate and
0.2 N Methyl Iodide

A = 40.00 B = 10.00 Temp. 35°

t.	x.	K.
20	1.62	0.00215
30	2.40	0.00220
40	3.11	0.00220
50	3.64	0.00211
60	4.20	0.00208

Average K = 0.00215

K_n = 0.04300

Table XXIV.

0.05 N Sodium Phenolate and
0.5 N Methyl Iodide

A = 400.00 B = 40.00 Temp. 35°

t.	x.	K.
45	17.96	0.00136
75	24.60	0.00132
90	27.50	0.00134
110	29.80	0.00130

Average K = 0.00133

K_n = 0.05320

Reactions between Sodium Phenolate and Ethyl Iodide at 25° and 35°.

Table XXV.

2 N Sodium Phenolate and
2 N Ethyl Iodide
A = 9.96 Temp. 25°

t.	x.	AK.
50	0.712	0.00154
60	0.86	0.00157
80	1.09	0.00153
95	1.285	0.00156
120	1.54	0.00153

Average AK = 0.00155

K_n = 0.00155

Table XXVI.

1 N Sodium Phenolate and
2 N Ethyl Iodide
A = 20.00 B = 10.00 Temp. 25°

t.	x.	K.
30	0.54	0.000937
50	0.86	0.000919
60	1.01	0.000912
70	1.19	0.000932
80	1.34	0.000932

Average K = 0.000926

K_n = 0.001952

Table XXVII.

0.5 N Sodium Phenolate and
2 N Ethyl Iodide
A = 39.92 B = 9.98 Temp.25°

t.	x.	K.
30	0.65	0.000566
45	0.96	0.000568
60	1.186	0.000534
70	1.33	0.000518
90	1.70	0.000529
115	2.18	0.000550

Average K = 0.000544

K_n = 0.002176

Table XXVIII.

1 N Sodium Phenolate and
1 N Ethyl Iodide
A = 10.00 Temp. 35°

t.	x.	AK.
30	0.876	0.00320
40	1.12	0.00315
50	1.34	0.00309
60	1.57	0.00310
70	1.79	0.00311
80	1.98	0.00309
100	2.32	0.00302

Average AK = 0.00311

K_n = 0.00622

Table XXIX.

0.5 N Sodium Phenolate and
0.5 N Ethyl Iodide
A = 9.98 Temp. 35°

t.	x.	AK.
50	0.82	0.00179
60	0.98	0.00181
80	1.25	0.00178
100	1.53	0.00181
120	1.79	0.00182

Average AK = 0.00180

K_n = 0.00720

Table XXX.

0.25 N Sodium Phenolate and
1 N Ethyl Iodide
A = 80.00 B = 20.00 Temp. 35°

t.	x.	K.
40	2.92	0.001006
60	4.14	0.000993
80	5.26	0.000988
100	6.36	0.000999
120	7.28	0.000993
140	8.20	0.000999

Average K = 0.000996

K_n = 0.007968

Tables of Conductivities.

Table XXXI.

Sodium Phenolate in Absolute Alcohol, 25°

Average values of three readings.

v	μ_v	μ_v/μ_∞
1	4.30	0.086
2	6.75	0.135
8/3	7.45	0.149
4	8.90	0.178
8	11.62	0.232
20	15.60	0.312
40	19.05	0.381

- - - - - - - - - - - - -

$\mu_\infty = 50.0$

Table XXXII

$$K_n = K_i\alpha + K_m(1 - \alpha)$$

V	K_n	
1	0.00766	$= K_i 0.086 + K_m 0.914$
2	0.00926	$= K_i 0.135 + K_m 0.865$
8/3	0.00976	$= K_i 0.149 + K_m 0.851$
4	0.01060	$= K_i 0.178 + K_m 0.822$
8	0.01176	$= K_i 0.232 + K_m 0.768$
20	0.01450	$= K_i 0.312 + K_m 0.688$

Table XXXIII.

Equations	K_m	K_i
V = 1: V = 2	0.0048	0.036
V = 1: V = 4	0.0049	0.036
V = 1: V = 8	0.0052	0.037
V = 1: V = 20	0.0051	0.034
V = 2: V = 4	0.0051	0.036
V = 2: V = 20	0.0052	0.035
Averages	0.0050	0.036

CONCLUSIONS.

I. An excess of phenol lowers the velocity of the reaction of sodium phenolate with alkyl halides for some reason not now known.

II. A method for the preparation of absolute alcohol has been developed and its specific gravity has been carefully determined.

III. Some physical properties of purified methyl iodide and ethyl iodide have been investigated.

IV. A comparison of different methods for making standard hydrochloric acid has been made.

V. A constant temperature pipette for transference of volatile liquids is described.

VI. A study has been made of the decrease of the velocity constants of alkyl halide reactions in long time-periods. It is shown that this cannot be due only to loss of alkyl halide from the reaction-flasks, but that other causes must be considered.

VII. When the velocities of the reactions in solutions having different concentrations are compared with the percentage dissociation of sodium phenolate in such solutions, measured by the conductivity method, it is found that both the phenolate ions and the sodium phenolate molecules (or the sodium ions and

phenolate ions together) react with the alkyl halide. In the reactions studied, the ions react about seven times as rapidly as the molecules.

Biography.

Henry Clarence Robertson, Jr., was born in Charleston, South Carolina, July 15, 1888. His preparatory training was received in private and public schools of Spartanburg, South Carolina.

In 1901 he entered Wofford College, Spartanburg, and graduated in 1905 with the degree of A.B. In the year 1906 he received the degree of Master of Arts from the same institution.

In October 1907 he entered the Johns Hopkins University as a graduate student in Chemistry, his subordinate subjects being Physical Chemistry and Biology.